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Anomalous In-Plane Anisotropy of the Onset of Superconductivity in $(TMTSF)_2ClO_4$

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We report the magnetic-field amplitude and field-angle dependence of the superconducting onset temperature T_c^{onset} of the organic superconductor $(TMTSF)_2ClO_4$ in magnetic fields $\boldsymbol{H}$ accurately aligned to the conductive ab' plane. We revealed that the rapid increase of the onset fields at low temperatures occurs both for $\boldsymbol{H} \parallel b'$ and $\boldsymbol{H} \parallel a$, irrespective of the carrier confinement. Moreover, in the vicinity of the Pauli-limiting field, we report a shift of a principal axis of the in-plane field-angle dependence of T_c^{onset}. This feature may be related to an occurrence of Fulde-Ferrell-Larkin-Ovchinnikov phases.

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Since the discovery of the organic superconductors $(TMTSF)_2X$ (where TMTSF stands for tetramethyl-tetraselena-fulvalene, $X = ClO_4$, PF_6, etc.) [1,2], their superconductivity has been widely studied. Because of the strong anisotropy in the electrical conductivity of these materials [3], they provide excellent opportunities to study the properties of quasi-one-dimensional (Q1D) superconductors. One of the most important and controversial issues on the superconductivity of $(TMTSF)_2X$ is the superconducting (SC) pairing symmetry [4]. In this Letter, we provide experimental results that contain new crucial clues to understand the SC symmetry of $(TMTSF)_2ClO_4$.

It has been suggested that the superconductivity of $(TMTSF)_2X$ is unconventional through the NMR relaxation time [5] and the impurity concentration dependence of the transition temperature T_c [6]. However, its SC symmetry is still controversial. One key feature of the SC symmetry is their unusually high upper critical fields $H_{c2}(T)$. Lee *et al.* [7] reported that $H_{c2}(T)$ of $(TMTSF)_2PF_6$ determined from resistivity diverges as temperature decreases and $H_{c2}(T)$ reaches up to 80 kOe at the lowest temperatures when magnetic fields $\boldsymbol{H}$ are applied parallel to the b' axis (perpendicular to the most conductive a axis in the ab plane). In this field direction, carriers are confined in the ab plane due to the field-induced dimensional crossover (FIDC) [4,8,9]. The FIDC suppresses the orbital pair-breaking effect and may allow the superconductivity to survive in higher fields. Interestingly, 80 kOe for $H_{c2} \parallel b'$ far exceeds the so-called Pauli-Clogston limit H_P [10], which fulfills a relation $H_P/T_c = 18.4$ kOe/K for an isotropic gap, where singlet Cooper pairs are unstable because unpaired carriers have a lower energy due to the Zeeman effect. In the case of Ref. [7], H_P was estimated to be 20 kOe. Similar results have been obtained in $(TMTSF)_2ClO_4$ by resistivity and magnetic torque measurements [11]. One interpretation attributes this survival of superconductivity above H_P to a spin-triplet state [12,13]. On the other hand, in Q1D superconductors, even singlet superconductivity can be stable far above H_P by forming a spatially modulating SC state [14,15], which is called the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state [16,17]. In 2002, Lee *et al.* [18] reported the absence of a change in the ^{77}Se Knight shift of $(TMTSF)_2PF_6$ at T_c under pressure, in favor of a triplet scenario. However, recently Shinagawa *et al.* [19] observed a clear change of the ^{77}Se Knight shift of $(TMTSF)_2ClO_4$ at T_c in lower fields. This finding motivated us to re-examine the possibility of singlet pairing in $(TMTSF)_2X$.

To resolve this puzzle, we are interested in the superconductivity in $\boldsymbol{H} \parallel a$ and its in-plane anisotropy. Although not much attention has been paid to the superconductivity for $\boldsymbol{H} \parallel a$ so far, data for $H_{c2}(T) \parallel a$ of $(TMTSF)_2PF_6$ [7] look quite interesting: it has a steep slope near $H = 0$ but saturates when it reaches H_P probably due to the Pauli effect, and it slightly increases again below 0.3 K. However, for $(TMTSF)_2ClO_4$ $H_{c2}(T) \parallel a$ was reported only above 0.5 K [20]. The in-plane anisotropy of H_{c2} of $(TMTSF)_2ClO_4$ was also reported but only at 1.03 K [20], where $H_{c2}(T)$ is far below H_P.

In the present study, we revealed the rapid increase of the onset fields not only for $\boldsymbol{H} \parallel b'$, where the electronic state becomes essentially 2D due to the FIDC, but also for $\boldsymbol{H} \parallel a$, where the electronic state remains anisotropic 3D. We also observed new features of the in-plane anisotropy developing above 20 kOe, which provide a crucial step to understand the origins of the enhancement of H_{c2}, in terms of FFLO states.

We used single crystals of $(TMTSF)_2ClO_4$ grown by an electrocrystallization technique, with dimensions of approximately $2.0 \times 0.2 \times 0.1$ mm^3. We report here the results of the sample with the highest T_c among up to 10 samples. We note that we obtained similar results in another sample. The resistance along the c^* axis R_{c^*} was measured using an ac four-probe method (the c^* axis is perpendicular to the ab' plane and is the least conductive direction) in a dilution refrigerator down to 80 mK. Temperature was measured using a RuO_2 resistance thermometer with magnetoresistance correction. Around 24 K, the anion ordering temperature of $(TMTSF)_2ClO_4$, a cooling rate as slow as 2 mK/ min, was chosen to ensure that the whole sample is in the "relaxed state."

Magnetic fields are applied using the "Vector Magnet" system [21], with which we can control the field direction without mechanical heatings. The directions of the orthogonal crystalline axes (the a, b', and c^* axes) of the sample were determined from the anisotropy of H_{c2} at 0.1 K. The accuracy of field alignment with respect to the ab' plane and of the a axis within the ab' plane are both better than 0.1°. We also determined the directions of the triclinic crystalline axes (the b and c axes) from angular magnetoresistance oscillations. The details of these procedures will be presented elsewhere. Hereafter, we denote the azimuthal angle within the ab' plane as ϕ which is measured from the a axis. We defined ϕ so that the b axis lies in the quadrant $0° < \phi < 90°$ as indicated in Fig. 1(a).

We first present $R_{c^*}(T)$ in zero field in Fig. 1(a). Although R_{c^*} of this sample started to drop at as high as 1.45 K and reached zero at 1.30 K, R_{c^*} increases again below 0.8 K. This increase, which is almost independent of magnetic fields, is probably attributed to small cracks in the sample. The data of $R_{c^*}(T)$ for $\boldsymbol{H} \parallel b'$ at 50 kOe are presented in Fig. 1(b). We observed a decrease of R_{c^*} below 0.2 K, consistent with a previous report [22]. In order to confirm that such a decrease is due to a superconducting contribution, we measured $R_{c^*}(T)$ after adding a small out-of-plane component $H_{c^*} = 0.5$–1.0 kOe to the magnetic field. If this decrease is due to the superconductivity, H_{c^*} should suppress the superconductivity and eliminate the decrease of $R_{c^*}(T)$. As plotted in Fig. 1(b), the decrease was indeed eliminated by adding H_{c^*}. Therefore, it was confirmed that the decrease of $R_{c^*}(T)$ is a contribution of the superconductivity. Then we evaluated the conductance difference $\Delta\sigma \equiv R_{c^*}^{-1}(H_{c^*} = 0) - R_{c^*}^{-1}(H_{c^*} > 0)$ and defined the onset temperature T_c^{onset} as the temperature at which $\Delta\sigma(T)$ exhibits a sharp increase, as marked by the small arrow in Fig. 1(b). This definition characterizes the very onset of superconductivity. We note that this anomaly in $\Delta\sigma(T)$ is not due to the normal state magnetoresistance, because it is unlikely that an abrupt change in $\Delta\sigma(T)$ occurs at a certain temperature. The definition has the advantage that T_c^{onset} is not affected by the extrinsic small increase of R_{c^*} because it is cancelled in the subtraction. For $\boldsymbol{H} \parallel c^*$, $T_c^{\mathrm{onset}}(H)$ was determined similarly from the conductance difference $\Delta\sigma(H) \equiv R_{c^*}^{-1}(H_{c^*} = H) - R_{c^*}^{-1}(H_{c^*} = H + \Delta H)$.

The phase diagrams for $\boldsymbol{H} \parallel a$, $\boldsymbol{H} \parallel b'$, and $\boldsymbol{H} \parallel c^*$ are presented in Fig. 2. In the vicinity of $H = 0$, linear temperature dependences of the curves were observed for all field directions. Within a GL theory for a clean type-II superconductor, with a tight-binding model, the slope $dH_{c2}(T)/dT$ at $T_c(H = 0)$ is related to the transfer integral t of each direction [23]. By taking into account the k_z dependence and the nodes of the gap over the Fermi surface (FS), we obtain $t_a = 1200$ K, $t_{b'} = 310$ K, and $t_{c^*} = 7.0$ K from the initial slopes indicated by the broken lines in Fig. 2. These values agree favorably with realistic band parameters [3]. From these analyses, it is clear that $H_{c2}(T)$ is governed by the orbital limitation at low fields in all three directions.

In higher fields, the behavior of these curves is qualitatively different. The curve for $\boldsymbol{H} \parallel b'$ keeps a linear T dependence up to 35 kOe and exhibits a rapid upturn in higher fields. This behavior is consistent with the "initial

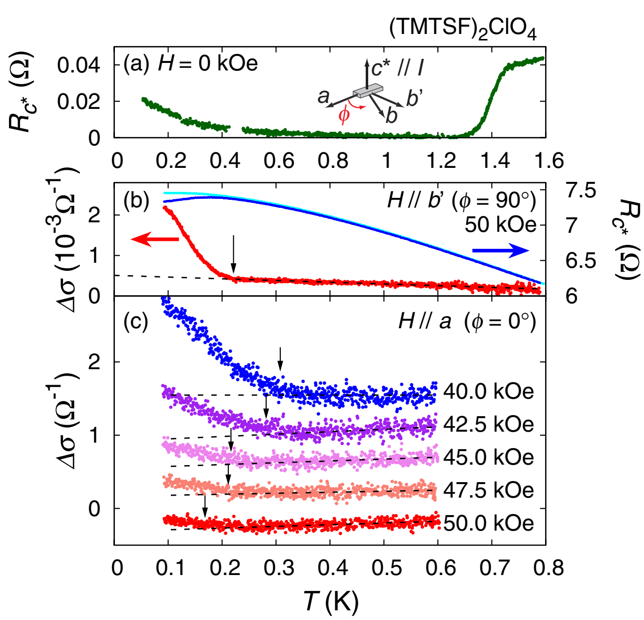

FIG. 1 (color online). (a) Temperature dependence of R_{c^*} in zero field. The directions of the orthogonal axes are illustrated in the inset. (b) Conductance difference $\Delta\sigma$ under an in-plane 50-kOe field applied parallel to the b' axis. Resistances for $H_{c^*} = 0$ kOe (blue curve) and $H_{c^*} = 0.5$ kOe (light blue curve) are plotted against the right vertical axis. (c) Temperature dependence of $\Delta\sigma$ with the in-plane field applied parallel to the a axis and $H_{c^*} = 1.0$ kOe. Some data are shifted vertically for clarity.

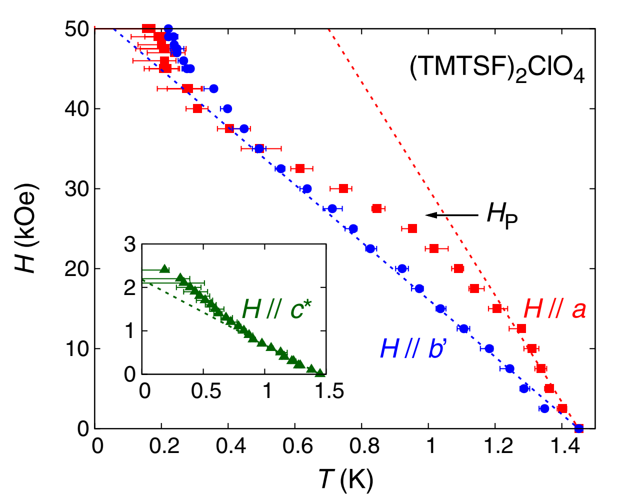

FIG. 2 (color online). Phase diagrams for $\boldsymbol{H} \parallel a$ (■) and $\boldsymbol{H} \parallel b'$ (●). The phase diagram for $\boldsymbol{H} \parallel c^*$ is shown in the inset. The broken lines indicate the initial slopes of each curves.

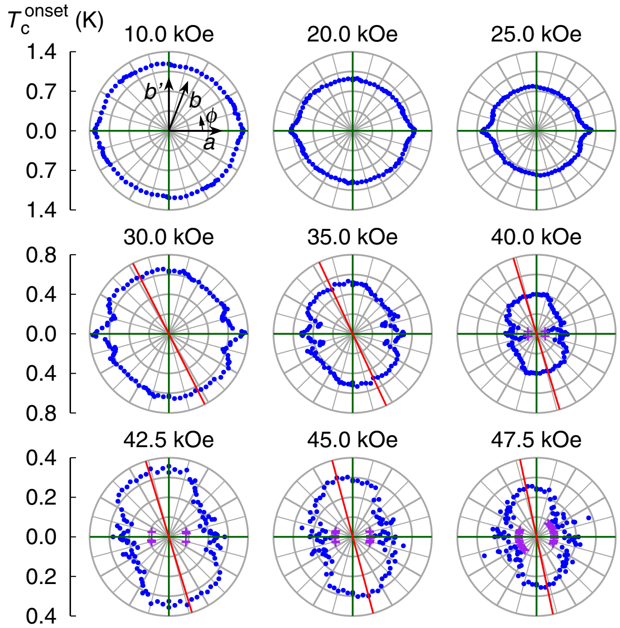

FIG. 3 (color online). Polar plots of $T_c^{\rm onset}(\phi)$. The points for $|\phi| > 90°$ are from the same data as those for $|\phi| \le 90°$. They are plotted in order to symmetrize the figure. Error bars are omitted for the sake of clarity. Purple crosses indicate that no SC anomaly in $\Delta\sigma(T)$ was observed above 80 mK. Solid red lines indicate the direction of the new principal axis $\boldsymbol{X}$.

cool'' curve in Ref. [11]. For $\boldsymbol{H} \parallel a$, the curve apparently shows limiting behavior; this is consistent with the Pauli-limiting behavior with the estimated value of $H_P = 26.7$ kOe. Interestingly, a small kink of $\Delta\sigma$ exists up to 50 kOe also for $\boldsymbol{H} \parallel a$, as shown in Fig. 1(c). Consequently, the onset curve diverges for $\boldsymbol{H} \parallel a$ at low temperatures, too. This is, to our knowledge, the first report of the low-temperature high-field phase diagram of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ for $\boldsymbol{H} \parallel a$. We note that we obtained similar phase diagrams for another sample. It is interesting that all three onset curves in Fig. 2 look similar to those for $(\mathrm{TMTSF})_2\mathrm{PF}_6$ [7].

Next, we focus on how $T_c^{\rm onset}$ changes when magnetic fields are rotated in the ab' plane. The data are displayed in Fig. 3 using polar plots of $T_c^{\rm onset}(\phi)$, where the direction of each point seen from the origin corresponds to the field direction and the distance from the origin corresponds to $T_c^{\rm onset}$. At low fields, $T_c^{\rm onset}(\phi)$ exhibits a sharp cusp at $\phi = 0°$ ($\boldsymbol{H} \parallel a$) and a broad minimum around $\phi = \pm 90°$ ($\boldsymbol{H} \parallel b'$). These low-field results are consistent with $H_{c2}(\phi)$ reported by Murata *et al.* [20], although the sharp peak at $\phi = 0°$ cannot be explained in an anisotropic 3D GL theory [24]. The chainlike crystal structure may play an important role in generating the sharp peak.

As the field increases above 20 kOe, dips of $T_c^{\rm onset}(\phi)$ emerge at $|\phi| = \phi_{\rm dip} = 17 \pm 1°$. We note that $R_{c^*}(T)$ in the normal state exhibits nonmetallic T dependence for $|\phi| > \phi_{\rm 3D\text{-}2D} = 19 \pm 1°$ above 20 kOe, signaling the onset of the FIDC [8,9]. Because $\phi_{\rm dip} \simeq \phi_{\rm 3D\text{-}2D}$, we infer that these dips are related to the FIDC. When the dimensionality of the electronic system is lowered, superconductivity in in-plane magnetic fields becomes more stable because the orbital pair-breaking effect is suppressed. Thus $T_c^{\rm onset}(\phi)$ should be enhanced for $|\phi| > \phi_{\rm 3D\text{-}2D}$, resulting in a minimum of $T_c^{\rm onset}(\phi)$ around $\phi_{\rm 3D\text{-}2D}$.

The most important anomaly is that in magnetic fields above 30 kOe, the b' axis is no longer a symmetry axis of $T_c^{\rm onset}(\phi)$ and a new principal axis $\boldsymbol{X}$ appears around $\phi \sim -70°$ as indicated by the solid red lines in Fig. 3. Moreover, behavior of $T_c^{\rm onset}(\phi)$ around $\boldsymbol{X}$, a principal axis at high fields, and b', a principal axis at low fields, is qualitatively different: at high fields $T_c^{\rm onset}(\phi)$ is *enhanced* around $\boldsymbol{X}$, while at low fields $T_c^{\rm onset}(\phi)$ exhibits a broad *minimum* around the b' axis. In addition, this $\boldsymbol{X}$ axis tends to rotate toward the b' axis as the field increases. At 47.5 kOe the deviation of $\boldsymbol{X}$ from the b' axis is reduced to about 10°. We checked that this change of symmetry is not due to a misalignment of the magnetic fields. In Fig. 4, we plotted the relative difference between $T_c^{\rm onset}(+45°)$ and $T_c^{\rm onset}(-45°)$ against the field strength. This quantity represents the asymmetry with respect to the b' axis; thus, the appearance of $\boldsymbol{X}$ results in finite values. Evidently, the asymmetry, i.e., $\boldsymbol{X}$, is absent in lower fields and then starts to develop around H_P. Therefore, the appearance of $\boldsymbol{X}$ cannot be attributed to conventional origins like an anisotropy of the Fermi velocity, because variation of $T_c^{\rm onset}(\phi)$ from such origins should develop from $H = 0$.

We now discuss the origin of the new principal axis $\boldsymbol{X}$, indicating the field direction in which $T_c^{\rm onset}(\phi)$ is enhanced. Its appearance should be related to the Pauli pair-breaking effect, because $\boldsymbol{X}$ appears at nearly H_P. In the case of singlet pairing, the appearance of $\boldsymbol{X}$ is attributable to the formation of an FFLO state [16,17], in which the Cooper pairs have a finite wave vector $\boldsymbol{q}_{\rm FFLO}$. In a Q1D superconductor, the stability of this state is greatly enhanced by the nesting properties of its FS [25] and that $\boldsymbol{q}_{\rm FFLO}$ essentially matches *the nesting vector between the spin-up and the spin-down FSs*, which should be nearly parallel to the a axis and should be independent of the field direction.

For $\boldsymbol{H} \parallel b'$, it has been discussed using orthorhombic band structures that an FFLO state with $\boldsymbol{q}_{\rm FFLO} \parallel a$ becomes stable with a help of the FIDC [14,15]. Although we are not

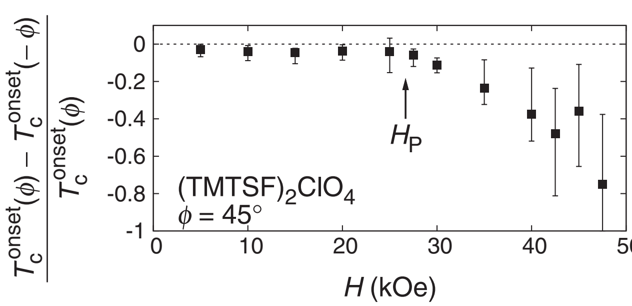

FIG. 4. Field dependence of the relative difference between $T_c^{\rm onset}(+45°)$ and $T_c^{\rm onset}(-45°)$.

aware of theories on the in-plane field-angle variation of this FFLO state taking into account the realistic triclinic band structure of $(TMTSF)_2ClO_4$, we expect that for $|\phi| > \phi_{3D\text{-}2D}$, where the FIDC takes place, this FFLO state is still stable. However, the direction of $\boldsymbol{q}_{FFLO}$, matching with the nesting vector, should be slightly tilted from the a axis because of the triclinic FS of $(TMTSF)_2ClO_4$. In addition, $\boldsymbol{q}_{FFLO}$ may vary with increasing the field because the separation between the spin-up and the spin-down FSs depends on $|\boldsymbol{H}|$. Within this scenario, one possible explanation of $\boldsymbol{X}$, which is the field-dependent special direction in the range $|\phi| > \phi_{3D\text{-}2D}$, is that $\boldsymbol{X}$ is perpendicular to $\boldsymbol{q}_{FFLO}$ and thus $\boldsymbol{H} \parallel \boldsymbol{X}$ corresponds to $\boldsymbol{H} \perp \boldsymbol{q}_{FFLO}$. Because the direction of $\boldsymbol{q}_{FFLO}$ is expected to depend on the field strength as we explained, $\boldsymbol{X}$ may also rotate in increasing field, consistent with our experimental results.

However, for $|\phi| < \phi_{3D\text{-}2D}$, namely, near $\boldsymbol{H} \parallel a$, the nature of superconductivity may differ from that near $\boldsymbol{H} \parallel b'$ because of the absence of the FIDC. Despite the absence of the FIDC, the orbital-limiting field is much larger than H_P near $\boldsymbol{H} \parallel a$ at low temperatures, which is evident from the steep slope of $H_{c2}(T)$ at $H = 0$ in Fig. 2. An FFLO state in a Q1D system in fields parallel to the most conductive axis has been proposed in a study of doped two-leg ladder cuprates using a t-J model [26]. We infer that a similar FFLO state might be stable near $\boldsymbol{H} \parallel a$, although a theory adapted to $(TMTSF)_2ClO_4$, a coupled chain system, needs to be developed. The recent NMR study, which reported that the density of states at the Fermi level recovers to the normal state value in the SC phase above 20 kOe for both $\boldsymbol{H} \parallel a$ and $\boldsymbol{H} \parallel b'$ [19], would support these FFLO scenarios.

On the other hand, if $(TMTSF)_2ClO_4$ is a triplet superconductor, polarized Cooper pair spins may cause an anisotropy of $T_c^{\mathrm{onset}}(\phi)$. Assuming that the spins of the Cooper pairs are fixed to one direction, superconductivity is not affected by a Pauli effect when the field is exactly parallel to the spins, while it is suppressed for the other field directions. In this case, however, it seems difficult to explain the rotation of $\boldsymbol{X}$.

In summary, we have studied the in-plane anisotropy of T_c^{onset} of $(TMTSF)_2ClO_4$. We observed that T_c^{onset} remains finite up to 50 kOe for $\boldsymbol{H} \parallel a$, as well as for $\boldsymbol{H} \parallel b'$. We suggest that the field-induced dimensional crossover plays an important role for the enhancement of T_c^{onset} when the field is tilted more than 17° from the a axis. In addition, one of the principal axes for superconductivity, which points along b' at low fields, shifts away from this direction around 30 kOe but evolves back toward the b' axis at higher fields. The survival of superconductivity far above H_P and the unusual in-plane anisotropy observed in the high-field regime suggest the stabilization of modulated superconducting phases when high fields are aligned to the ab' plane, in favor of a spin-singlet scenario. We speculate that two kinds of FFLO states are realized in this compound: the one predicted by Dupuis *et al.* [15] near $\boldsymbol{H} \parallel b'$ and the one related to the prediction by Roux *et al.* [26] for $\boldsymbol{H} \parallel a$, separated by the dips of $T_c^{\mathrm{onset}}(\phi)$ around $\phi \sim \pm 17°$. We believe that theoretical studies taking into account the triclinic band structure are desirable to understand our results and reveal the SC symmetry of $(TMTSF)_2X$.

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